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Homogenizing Sludge Produces Unexpected Mercury Results

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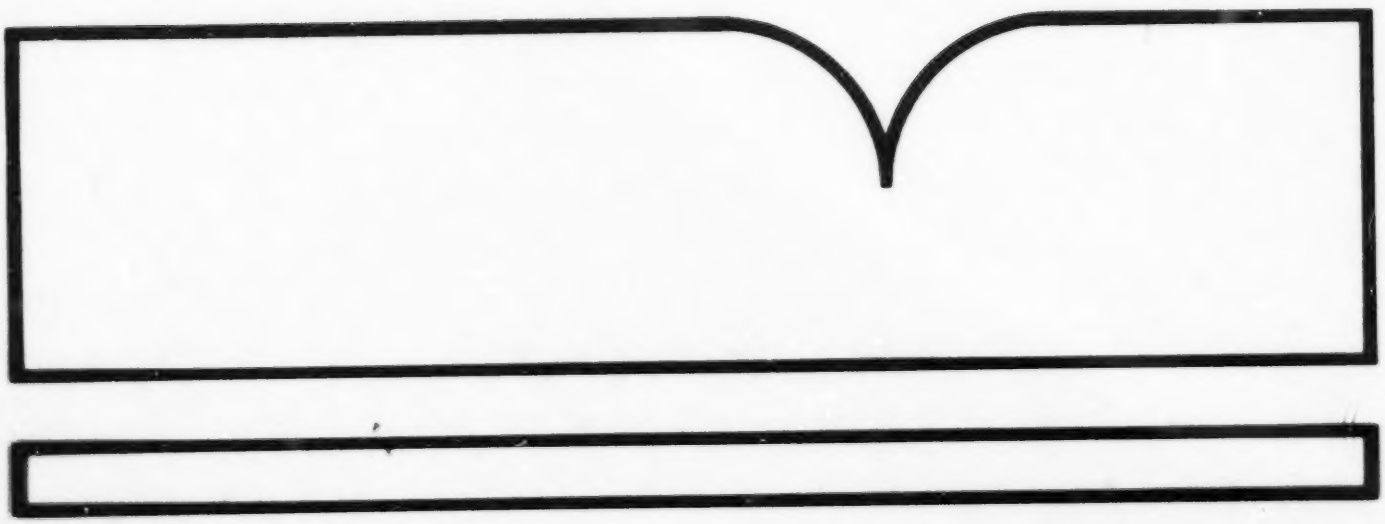

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16. ABSTRACT

A method to homogenize sewage sludge prior to analysis for mercury and other trace elements is described.

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Homogenizing sludge produces unexpected mercury results

W J MITCHELL, M R MIDGETT, J SUGGS, R J VELTEN and D ALBRINCK

U.S. Environmental Protection Agency (EPA) regulations limit atmospheric emissions of mercury (Hg) from sewage sludge incineration plants to 3200 g/24-hr day. These emissions can be measured either directly by means of a stack test or, as is usually done, indirectly by a sludge analysis using EPA Method 105.[1] The analysis is done on three sludge samples collected over a 24-hr period with each sample representing a composite of eight consecutive 200- to 400-mL grab samples collected at 1-hr intervals. However, dewatered sewage sludge samples cannot be reliably homogenized, at least for mercury analysis, by manual mixing alone. But a reliable homogenization can be obtained using a commercially available mortar mixer.

In March 1977, a collaborative test of EPA Method 105 was conducted with ten laboratories analyzing grab samples of dewatered sludge from three sludge treatment plants. Grab rather than composite samples were used to minimize the effect of sample nonhomogeneity on the results, since Method 105 is concerned only with sample analysis and not with sample collection. Each 150-g grab sample was manually mixed for 15 min and divided into 10-g portions. Each laboratory received a 10-g portion from each plant, dried each sample and then digested and analyzed it in triplicate using EPA Method 105.

To provide an alternate determination of Hg content, an EPA laboratory analyzed a portion of each grab sample in duplicate using neutron activation analysis (NAA). The results of the collaborative test showed clearly that for a given sample, agreement between laboratories and, at times within laboratories, was poor, Table 1.

A statistical analysis of the results indicated that nonhomogeneity in mercury concentration was a significant cause of the within-sample variation in at least two of the three samples, an indication that hand-mixing was not an effective way to homogenize sludge samples for mercury analysis. This finding was important because Method 105 normally would be used on a composite sludge sample composed of either grab samples, and the regulations do not specify any sludge mixing procedure for this composite sample.

Development of a homogenizing procedure

Various sludge mixing procedures were evaluated by adding zinc oxide to 27 kg of dewatered sludge and analyzing for Hg and zinc as a function of mixing time. It was found that a 57-L (2 ft³)-capacity wheelbarrow-type commercial mortar mixer rotating at 30 rpm for 30 min would effectively mix sludge samples. Mixing times less than 30 min were inadequate.

The effectiveness of this mixing technique was then verified using time-composite dewatered sludge samples from three sludge treatment plants. At the same time a study was conducted to determine the optimum sampling interval for collecting samples for the time-composite (bulk) sample. To accomplish this, the sludge conveyor line was sampled over an 8-hr interval in such a way that 27-kg bulk samples comprising grab samples taken at

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Table 1. Collaborator results on sewage sludge samples, μg Hg/g dried sludge

Sample	NAA results	Method 105 results									
		Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9	Lab 10
1	1.8	3.8	2.8	2.8	0.66	1.0	3.1	1.4	1.2	*	0.33
	3.9	3.3	2.7	2.8	0.82	1.5	3.1	1.2	1.6	*	0.45
		0.87	2.8	3.7	0.91	1.0	3.5	1.2	1.4	*	0.63
2	3.0	4.1	2.5	2.7	0.57	1.1	1.8	10	1.5	*	0.18
	2.2	2.7	2.3	2.9	0.48	1.6	2.0	12	1.4	*	*
		1.0	2.3	3.6	0.45	5.1	2.2	13	1.3	*	0.94
3	2.3	3.8	3.0	2.6	0.71	2.0	3.3	2.3	2.7	*	0.49
	2.4	3.9	2.9	2.8	1.1	3.8	3.3	1.9	2.7	*	0.82
		0.79	3.0	3.5	1.6	2.2	3.8	2.3	2.7	*	*

*No Hg detected.

different intervals would be collected. For example, one bulk sample might be composed of 0.3-kg grab samples collected at 5-min intervals. Another might be composed of 1.0-kg samples collected at 15-min intervals. Sampling intervals of 5, 10, 15, 20, 25, 30 and 60 min were used in this study, although not all of these were used at every plant.

Each 27-kg sample was taken to the laboratory where the entire quantity was placed in the mortar mixer and mixed for at least 30 min at 30 rpm. Two to four 500-mL samples were then withdrawn from the mixer and each was blended in a 2-L home-type blender for 2 min. Three to five 20-mL sludge samples were then withdrawn from the blender and transferred to separate tared 125-mL Erlenmeyer flasks which were reweighed to obtain the exact weight of sludge added. Twenty-five mL of aqua regia was added to each sample, which was then digested at low temperature for 30 min on a hot plate, cooled, filtered through S and S No. 588 filter paper, diluted to 100 mL and analyzed for Hg using the following apparatus and analytical procedure.

Mercury analysis procedure

A 5- to 25-mL aliquot of the digested sample was added to 25 mL of distilled, deionized water in an aeration bottle. Three drops of Baker Antifoam B Silicone Emulsion were added, followed in sequence by 5 mL of 15 percent (V/V) nitric acid and 5 mL of 5 percent (by weight) potassium permanganate. The solution was then mixed well using a magnetic stirring bar. A solution, prepared by dissolving 12 g of sodium chloride and 12 g of hydroxylamine sulfate in 100 mL of distilled, deionized water was then added in 5-mL aliquots and stirred until a clear solution was obtained. Five mL of 10 percent (by weight) stannous chloride[2] was added to the aeration cell and the mercury aerated into the atomic absorption cell using nitrogen as the purge gas. Selected samples were also spiked and reanalyzed (Method of Standard Additions[3]) to confirm the accuracy of the original analysis. The spectrophotometer calibration standards were prepared as directed in EPA Method 105, but the actual analytical procedure used here differed from that described in Method 105[1] to accommodate the 20-fold increase in size of the sludge sample taken for analysis in this study compared to that now specified in Method 105.

Unexpected results of the program

Table 2 summarizes the results obtained at each sludge treatment plant in relation to frequency of sludge removal from the conveyor belt over an 8-hr interval (bulk sample), number of 500-mL samples withdrawn from the mortar mixer, number of aliquots analyzed from each blended 500-mL sample, and the grand mean (μg Hg/g dried sludge) for each bulk sample. During this study, a total of forty-eight 500-mL samples were taken from 18 bulk (27 kg) samples and at least three analyses were performed on each 500-mL sample after blending.

A comparative statistical analysis on all results showed that: (1) all 20-mL aliquots from a 500-mL sample were statistically identical; (2) all 500-mL aliquots from a bulk sample were statistically identical with the exception of one sample from Plant 1; but (3) bulk samples from the same plant were not always statistically identical. For example, the 10- and 20-min interval samples from Plant 3 (July 1978) are not statistically the same as the other four bulk samples. Analogously, the 5-, 15- and 30-min interval samples from Plant 1 are statistically the same, but the 60-min interval sample is statistically different from the 5- and 15-min interval samples.

This shows that the bulk sludge samples were effectively homogenized but the actual Hg content of the bulk samples was affected in a nonpredictable manner by the sampling frequency. Although the cause of this time variation has not been specifically identified, it seems likely that it was caused by each plant having at least two processes depositing sludge on the conveyor belt at the same time but on an intermittent basis; e. g., sludge would be deposited at 2- to 10-sec intervals. Further, the amount of sludge deposited at any one time also varied within a process. If this was the cause, then it seems likely that a similar variation will occur when the sludge line is sampled to determine the amount of other trace elements present. Since this variation would result from the process itself, the simplest way to minimize its effect on the analytical results might very well be to collect a large bulk sample that is composed of many grab samples; e. g., grab samples taken no farther than 15 min apart.

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Table 2. Effect of sampling frequency on mercury results

Sampling date	Plant No.	Number of 500-mL samples from each bulk sample	Number of 20-mL aliquots from each 500-mL sample	Mercury content (μg Hg/g dried sludge) in each bulk sample						
				5-min	10-min	15-min	20-min	25-min	30-min	60-min
1/78	1	2	5	1.28	–	1.19	–	–	1.57	1.87
2/78	2	2	5	2.88	–	2.95	–	–	2.61	3.33
4/78	3	2	5	2.65	–	2.12	–	–	2.92	3.25
7/78	3	4	3	4.78	4.01	4.82	5.40	4.46	4.50	–